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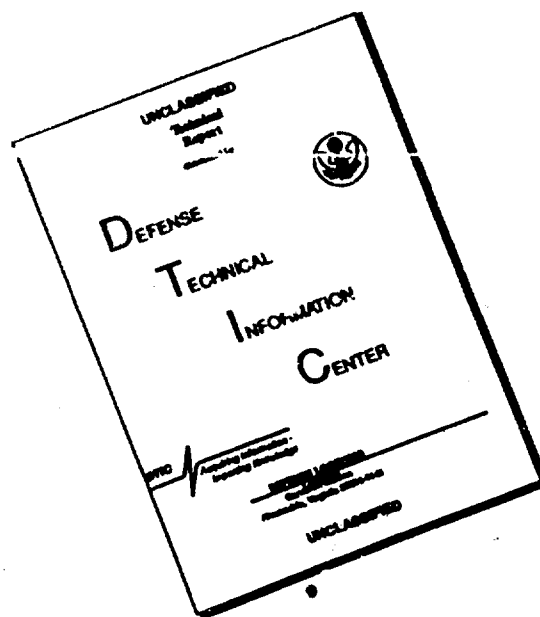DEPARTMENT OF THE ARMY
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INVESTIGATIONS OF THE SURFACE LAYER OF LIQUID SYSTEMS

VII. SURFACE DEMIXING AND VOLUME PROPERTIES OF SOLUTIONS OF BINARY SYSTEMS

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Surface demixing in binary liquid systems [1] is due, in the final analysis, to the same factors as volume demixing. There have been objections to this [2], which consisted of the view that demixing in the surface layer while the solution retains its homogeneity in the bulk is thermodynamically impossible.

We will show that in binary systems, under definite conditions, surface demixing is as inevitable thermodynamically, as is demixing in the volume of the solutions.

Let us examine a system formed by the liquids A and B, of limited solubility. In Fig. 1 the solubility curve is represented by a continuous line. Let the surface tension of the first component be greater than that of the second, or $\sigma_A > \sigma_B$. In that case the concentration $\underline{x}$ of component B is greater in the surface layer than N, the concentration in the volume of the solution.
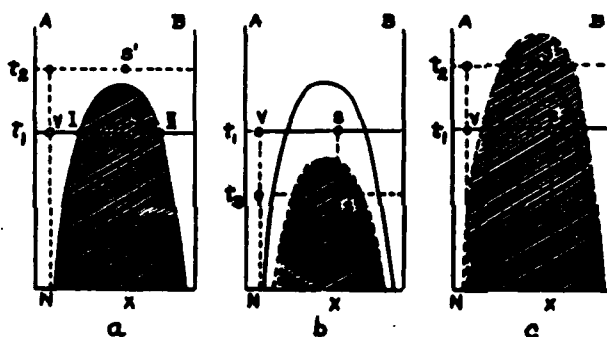

Fig. 1. Relationship between the regions of volume and surface demixing in a system with an upper critical point (the region of surface demixing is shaded).

a) In the first of the three possible cases let us assume the activity coefficients in the surface layer and in the volume of the solution to be equal. In this case, a point $\underline{z}$ in the surface layer will correspond to, say, a solution given by the point $\underline{v}$, at the temperature t_1. But at the given temperature in the system in question the existence of a solution with concentration $\underline{x}$ is thermodynamically impossible, and it inevitably separates into two solutions I and II. Thus, a heterogeneous surface layer should correspond to a completely homogeneous solution. It is evident, however, that at a temperature above the critical solubility point, for example t_2, a homogeneous surface layer of concentration $\underline{x}'$ (the point $\underline{z}'$) corresponds to the same solution.

b) The case when, due to peculiarities of orientation of the molecules, the activity coefficients of the components are greater in the surface layer than in the volume of the solution, so that their mutual solubility in the surface layer is greater (the corresponding curve in Fig. 1, b is shown by a broken line; the critical solubility point is at a lower temperature). In this case a surface layer composition represented by the figurative point $\underline{z}$, which lies outside the demixing zone in the surface layer, corresponds to the solution considered previously; hence, a homogeneous surface layer corresponds to this solution. Only at a lower temperature, for example t_3, is the figurative point $\underline{z}'$ for the surface solution found in the region of demixing.

c) In the third possible case the activity coefficients of the components in the surface layer, due to orientation peculiarities in this case also, are greater than in the solution volume. The mutual solubility of the components in the surface layer then becomes less, and the corresponding curve (broken line in Fig. 1, c) lies at higher temperatures. In this case, surface demixing should take place not only at the temperature t_1, at which the liquids have limited solubility, but at the temperature t_2, at which no demixing takes place in the volume of the solution.
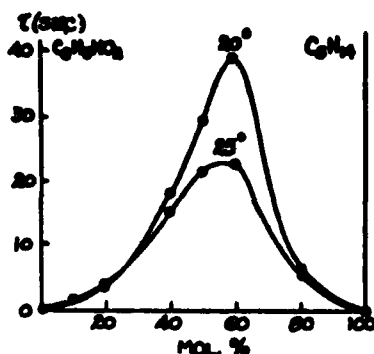
Fig. 2. Isotherms for foam stability in the system nitrobenzene—n-hexane.

Thus, surface demixing must inevitably occur in definite cases, and it is the cause of certain anomalies in the variation of the surface tension of solutions with temperature.

It is interesting to note that such anomalies, known previously in aqueous solutions of sparingly soluble substances [3] and in solutions of organic liquids with a tendency to demixing [4, 5], were recently noted in a completely new field, namely in metallic melts. Thus, in the systems Ag—Pb and Ag—Bi, which have a tendency to demixing in the liquid state and which have negative heats of mixing, Metzger [6] found a positive value of $\delta\sigma/\delta T$ over a wide range of concentrations and temperatures. In addition, we can cite a new example of surface demixing in systems of organic liquids, the system $C_6H_5NO_2-C_6H_{12}$.*

The system nitrobenzene—n-hexane in many respects resembles other systems of nitrobenzene with hydrocarbons, in which we observed surface demixing. There were reasons for expecting surface demixing to occur in this system also.

The properties of the nitrobenzene used were given in our earlier work [5]. The hexane, after drying over metallic sodium, distilled in the range 67.7-67.8° at 748 mm, and had density d^{20} 0.6603. The solutions of the system form a foam on shaking. The stability of the foam, determined by the same method as for the systems previously studied, is shown in Fig. 2. The maximum foam stability is given by a solution containing 60 mol-% of hexane.

The results of surface tension measurements are shown in Fig. 3. As was to be expected, the course of the polytherms for surface tension is quite analogous to the course of the polytherms in many of the systems of nitrobenzene or aniline with hydrocarbons studied by us. As in the system nitrobenzene—n-octane, we observe a practically unchanged value of σ over a considerable range of temperatures for solutions containing 25 and 30 mol-% hexane. We explain such peculiarities of the dependence of surface tension on temperature by the assumption of surface demixing in the system.

With the aim of correlating the temperature variations of surface tension with variations of certain volume properties, we carried out measurements of the dielectric constant of solutions of this system, and also of solutions of cyclohexane in aniline, repeating the measurements reported in the paper by Starobinets, Fisher, and Milchina [?].
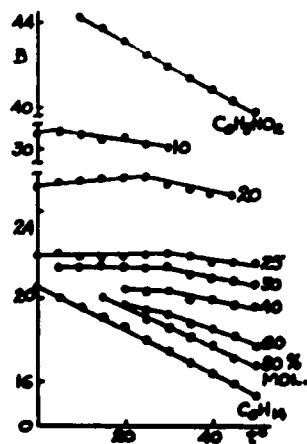

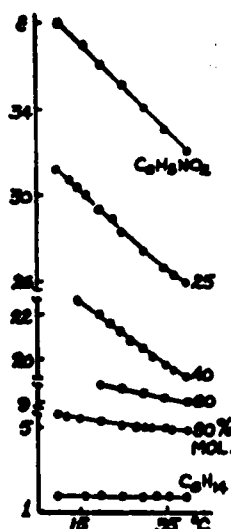Fig. 3. Polytherms for surface tension of solutions in the system nitrobenzene—n-hexane.

Fig. 4. Polytherms for the dielectric constant of solutions in the system nitrobenzene—n-hexane.

The measurements of the dielectric constant were carried out by the resonance method in conjunction with the substitution method. The instant of tuning the generators into resonance was determined with greater accuracy by the method of beats with the aid of the 6E5 optical indicator. The measurements were made at a frequency of 500 kilocycles/sec. The fluid capacitor had an air capacity of 7580 μμF. The solution being measured was isolated from the air in the measuring capacitor and kept at a constant temperature to an accuracy of $\pm$ 0.1° by means of a water jacket.

The results obtained for the system nitrobenzene—n-hexane are shown in Fig. 4. These results show that there is a regular decrease of dielectric constant as we pass from nitrobenzene to hexane —liquids which greatly differ in their values of ε. We also note the high temperature coefficient of the dielectric constant for nitrobenzene (which is due to its large dipole moment), and a very low one, close to zero, for hexane. The temperature coefficient for the solutions has intermediate values.

The polytherms for ε for the solutions are smooth lines, nearly straight, and do not show any "inflexions" or other anomalies. Consequently, the transformations which take place in the surface layer, and which are clearly shown on the surface tension polytherms, are not found on the dielectric constant curves,.
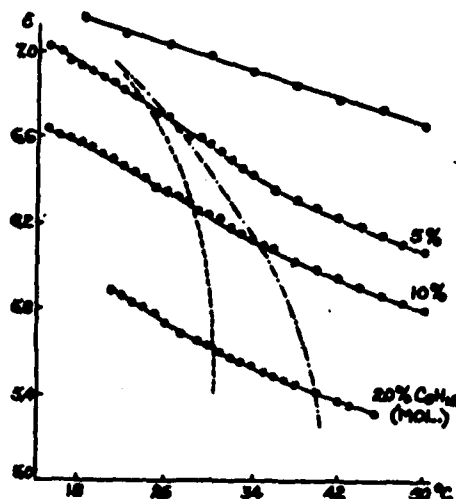

Fig. 5. Polytherms for the dielectric constant of certain solutions in the system aniline—cyclohexane. The top curve represents $C_6H_5NH_2$.

As regards the measurements of the dielectric constant for the system aniline—cyclohexane, these were made with special care, as the aim was to verify the data already published in the literature. The determinations were made at intervals of 1, and more rarely of 2°. The results of the measurements are shown on a very large scale in Fig. 5. Examination of these results shows that the dielectric constant of the solutions shows smooth variations. Although the value of the temperature coefficient of the dielectric constant of the solutions varies with temperature, it is not possible to find on the polytherms any of the "inflexions" reported by Starobinets, Fisher, and Milchina. A broken line on the graph represents the line which these authors draw through the "points of inflexion" from their results for dielectric constant [2]. The dot-and-dash line represents the boundary of surface demixing of the solutions from surface tension measurements [4]. As we see, the dielectric constant curves do not show any deviations of their course at the corresponding temperatures.

Consequently, from dielectric constant measurements it is not possible to report objectively any sudden changes of the structure of the solution (in its volume) at the temperatures of surface demixing.

If variations of structure take place in the solutions, they must inevitably be reflected in the value of the density, which is a fundamental property. This reasoning led us to carry out a dilatometric investigation of certain solutions in the systems previously studied, in the temperature range where surface demixing is observed.

A dilatometer of about 6 ml capacity was used, with a long calibrated neck 1 mm in diameter. The apparatus was immersed in a water thermostat (the temperature was maintained constant to an accuracy of $\pm$ 0.02°), and the

liquid level in the dilatometer neck was determined with the aid of a cathetometer. By this means, density variations could be measured with an accuracy of $\pm 1 \cdot 10^{-5}$. In addition to the main series of measurements, which included a full heating and cooling cycle, repeat measurements were also carried out on the same solutions at various temperatures (when temperature readings were taken, the dilatometer was held for 15-20 minutes until all displacement of the meniscus completely ceased).

The results of determinations on solutions of 20 mol-% cyclohexane + 80 mol-% aniline, and 20 mol-% methanol + 80% mesitylene are shown in Fig. 6. In both cases, the experimental points lie well on a smooth line, very nearly straight. There are no inflexions or deviations from this line. This indicates that the coefficient of volume expansion varies smoothly, and consequently proves convincingly the absence of structural transformations in the volume of the solution at any definite temperature in the range investigated.
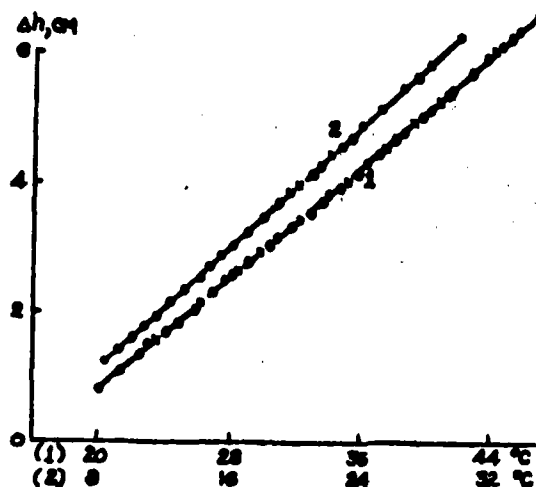

Fig. 6. Dilatometric curves for the solutions: 1) 20 mol-% cyclohexane + 80% aniline; 2) 20 mol-% methanol + 80% mesitylene; ● = heating; o = cooling; + = repeated heating; Δh = height of the liquid level in the dilatometer neck.

Thus, in the cases examined, surface tension measurements disclose effects which do not extend to the whole bulk of the solution and appertain only to the surface layer. The demixing, which is found in the surface layer from the data of surface tension measurements, occurs in the volume of the solution, inevitably on thermodynamical grounds, in different circumstances=at different temperatures and concentrations. Both the effects, however, are due to the same causes. Therefore, there are no reasons for seeking any new causes (for example, structural transformations in the solution) in order to explain the nature of the anomalies which are observed in surface tension measurements.

SUMMARY

1. An analysis is presented of the possible relationships between the regions of volume and surface demixing in the coordinates: temperature-concentration. Surface demixing is shown to be thermodynamically inevitable.

2. The surface tension and foam stability in the system nitrobenzene—n-hexane has been studied polythermally. The results indicate the existence of surface demixing in this system.

3. Polythermal measurements of the dielectric constant have been carried out on the same system, and also on solutions of cyclohexane in aniline. Two solutions were studied dilatometrically: 20 mol-% cyclohexane + 80% aniline, and 20 mol-% methanol + 80% mesitylene.

4. The polytherms of the volume properties studied do not show any anomalies at temperatures corresponding to surface demixing.

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